



⑫

EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of patent specification: **08.06.94** ⑮ Int. Cl. 5: **C08J 9/24, C04B 35/52, C08L 61/06**
 ⑯ Application number: **87306479.4**
 ⑯ Date of filing: **22.07.87**

The file contains technical information submitted after the application was filed and not included in this specification

⑯ **Process for the production of porous shaped articles.**

⑯ Priority: **22.07.86 GB 8617831**

⑯ Date of publication of application:
27.01.88 Bulletin 88/04

⑯ Publication of the grant of the patent:
08.06.94 Bulletin 94/23

⑯ Designated Contracting States:
BE CH DE ES FR GB IT LI NL SE

⑯ References cited:
DE-A- 1 471 364 DE-A- 2 623 828
GB-A- 1 330 296 US-A- 2 611 750
US-A- 2 611 750 US-A- 3 288 745

⑯ Proprietor: **THE BRITISH PETROLEUM COMPANY P.L.C.**
Britannic House,
1 Finsbury Circus
London EC2M 7BA(GB)

⑯ Inventor: **Satchell, Paul Wayne**
BP Chemicals Limited
Sully
South Glamorgan Cf6 2YU Wales(GB)
 Inventor: **Lear, Anthony Martin**

The British Petroleum Co., p.l.c
Chertsey Road
Sunbury-on-Thames Middlesex TW16
7LN(GB)
 Inventor: **Tennison, Stephen Robert**
The British Petroleum Co., p.l.c
Chertsey Road
Sunbury-on-Thames Middlesex TW16
7LN(GB)

⑯ Representative: **Preece, Michael et al**
BP International Limited
Patents and Agreements Division
Sunbury Research Centre
Chertsey Road
Sunbury-on-Thames, Middlesex TW16 7LN
(GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

The present invention relates to the production of shaped porous phenolic resin and carbon articles with improved strength.

5 Porous phenolic resin articles may be used for example as filters or membrane supports.

Porous carbon articles can be used for:

- (a) catalyst supports of various shapes (e.g. raschig rings),
- (b) shaped electrodes for electro-catalysts,
- (c) carbon composites
- 10 (d) engineering carbon artefacts (e.g. crucibles),
- (e) high temperature thermal insulators.

GB-A-1 130 829 discloses the production of carbon articles with a predetermined shape by moulding. Ground coke is mixed with a carbonisable aromatic binder e.g. pitch. The mixture is then formed into the desired shape, the binder is carbonised, and the resulting product further heated. However, the pitch used 15 as binder in the above process will tend to fill up the spaces between the coke particles so making the product difficult to carbonise. In addition the internal porosity of the coke particles may become partly filled up by the pitch, leading to low porosity products.

It is well known that activated carbon can be produced in the form of pellets by carbonising pellets of 20 organic material e.g. wood chips. However, the mechanical strength of such pellets is relatively low, even after carbonisation at high temperature.

WO-A-81/03167 discloses the production of a porous carbon by depositing particles of carbonisable polymer is such a way that the particles produce a regularly packed deposit. This is partially degraded to make it form stable, and then heated to carbonise it.

US-A-4 263 268 shows the preparation of porous carbon from a phenolic resin which is deposited within 25 the pores of an inorganic material. The resin is polymerised within the pores, the inorganic material is removed, and the resin pyrolysed to form carbon. The resulting carbon is very porous but has a very poor mechanical strength. The fragility of the product is specifically mentioned in the specification.

GB-A-1 330 296 discloses the formation of carbonised materials from powdered phenolic resins. However, the resins are specifically stated to be thermoplastic resins. We have attempted to repeat the 30 process of GB-A-1 330 296. We have not found it possible to make strong porous articles or articles with shape stability.

US-A-2 611 750 discloses the production of porous phenolic resin products from partially condensed phenolic resin in an intermediate plastic solid stage with the consistency of set gelatine or an elastic solid, and thus with a low degree of cure. The degree of condensation is so low that particles are formed by 35 stirring and not by grinding.

DE-A-1 471 364 discloses the production of a carbon article from phenolic resin. However, the carbon is non-porous and there is nothing to suggest that the resins are not conventional thermoplastic resins.

We have now found a method of producing porous shaped article having improved strength, with continuous open pore structure.

40 According to one aspect of the present invention the process for the production of a shaped porous phenolic resin article with a continuous open pore structure which comprises:

- (a) partially curing a phenolic resin to a solid,
- (b) grinding the solid to form particles,
- (c) forming the resulting ground product to a pre-determined shape at a pressure in the range 0 to 800 45 MPa,
- (d) sintering the shaped solid so as to produce a form-stable sintered product,

the temperature and duration of the partial curing step (a) being so selected as to give a degree of cure sufficient to give a sinterable product, and being such that a sample of the partially cured solid when ground to produce particles in the size range 106-250 micrometres and tabletted in a tabletting machine 50 gives a pellet with a crush strength which is not less than 1 N/mm.

According to another aspect of the present invention the process for the production of a shaped porous carbon article with a continuous open pore structure which comprises forming a shaped porous phenolic resin article as defined above, and carbonising the shaped porous phenolic resin article, the temperature and duration of the partial curing step (a) as defined above being such that the pellet after carbonisation has 55 a crush strength of not less than 8 N/mm.

By "sintering" we mean a step which causes the individual particles of phenolic resin to adhere together without the need for a separately introduced binder, while retaining their individual identity to a substantial extent on heating to carbonisation temperatures. Thus the particles must not melt after forming

so as to produce a molten mass of resin as this would eliminate the internal open porosity of the article. The open porosity (as opposed to the closed cells found in certain types of polymer foams) is believed to be important in enabling formed articles to retain their shape on carbonisation.

Phenolic resins are well known materials. They are made by the reaction of a phenol and an aldehyde

5 e.g. formaldehyde. The condensation is initially carried out to produce a partially condensed product. The condensation may be carried out so as to produce a resin which is fully curable on further heating. Alternatively the condensation may be carried out so as to produce a novolak resin which is only curable when an additional cross-linking agent is mixed with it e.g. hexamethylene tetramine (known as "hexamine" or "hex"). It is preferred to use hexamine-cured novolak resins in the process of the present invention.

10 In order to produce comminuted resin which can be sintered satisfactorily it is necessary to control the temperature and duration of the partial curing step, and the quantity of any cross-linking agent used. If the resin is grossly undercured then no sintering step will be possible because the comminuted particles will melt under the conditions used to form the pre-determined shape. The degree of partial cure may be sufficient that sintering (as defined herein) takes place on directly heating the comminuted resin without any 15 additional additives.

Alternatively the degree of partial cure may be such that sinterable material is obtained after the addition of additional cross-linking agent in a post-curing step. If the resin is overcured it will not be possible to sinter the comminuted particles because they will not adhere together.

20 The degree of cure of the resin before it is comminuted is critical. The resin must be substantially cross-linked and thus at a higher degree of cure than in the typical commercial phenolic resin moulding powder. If the degree of cure is too low the shaped product formed from the comminuted resin will melt during sintering or carbonisation. If however the resin is fully cured then the sintering step cannot be carried out satisfactorily and the final phenolic or carbon product will have very low strengths.

25 The degree of partial cure is preferably such as to give a certain minimum strength in the shaped article before and after carbonisation.

30 The strength of a sintered article is also dependent on the size of the particles sintered together. Large particles give reduced strength. Thus when evaluating the conditions giving a given degree of partial cure by means of the strength of the resulting article it is desirable to use a standard particle size range. It is preferred to use comminuted resins particles in the size range 100 to 250 micrometres when preparing samples for evaluating degree of cure by means of strength testing.

For instance when producing cylindrical articles on a tabletting machine from comminuted partially cured resin of particle size 106-250 micrometres, the diametric crush strength of the pellets before carbonisation preferably does not fall below 1 N/mm (0.1 kg/mm) and the diametric crush strength of the carbonised pellets preferably does not fall below 8 N/mm (0.8 kg/mm).

35 The diametric crush strength referred to throughout this specification is a normal test within the tabletting industry and expresses the force required to crush a pellet across its diameter as a function of the length of the pellet which is bearing the load.

40 Two pieces of apparatus have been used. A Manesty Monsanto tablet hardness tester which measures crush forces up to 8.5 kg has been used and an Instron has been used for measuring crush strengths from 1 kg upwards. The method consists of measuring the length of a pellet and then crushing the pellet across its diameter between two perfectly flat metal surfaces. A value in N/mm (kg/mm) is calculated. This is repeated for a number of pellets and a mean value calculated.

45 For any given resin composition the degree of cure is determined by the curing agent (eg hexamine) content and dispersion and the temperature and duration of the curing step. Thus if 5 to 10% of finely ground hexamine is thoroughly mixed with finely ground resin then the temperature of the partial curing step is preferably below 150 °C. If, however, less than 5% hexamine is used then higher temperatures can be used.

50 The prior art does not teach that the degree of cure is critical in the production of carbonised articles from phenolic resins. However, once the invention has been disclosed to a skilled person as in the present specification, such a person will have no difficulty in carrying out tests to determine the degree of cure by making shaped articles from comminuted resin made with varying degrees of cure. Degree of cure can also be determined by carrying out studies using differential scanning calorimetry. For samples cured to various extents, glass transition temperature increases and the exotherm due to the completion of the cure decreases with increasing extent of cure.

55 The partial curing step may be conveniently carried out so as to produce slabs of resin which are then comminuted. Conventional grinding machinery may be used to comminute the resin. The resin may be reduced to powder for example with a particle size of less than 500 micrometres, for example 45-250 micrometres. The macropore structure of the final article can be controlled by altering the particle size

distribution of the resin at this stage. The use of mixed particle sizes will result in a lower macropore volume. For instance, fine particles of less than 50 micrometres produced by cryogenic grinding could be added to a larger particle size distribution.

The comminuted particles are then formed into shaped articles. This may be done under pressure for

5 example by conventional tabletting or pelleting equipment. Shaped articles may be produced without pressure e.g. by using vibration to ensure that a mould is adequately filled with particles. In addition the resin powder may be moistened with a suitable liquid (for example water) to enable extrusion to be carried out or to allow easier pressing into shapes. Examples of pressures which may be applied in such a forming step are 0 to 800 MPa.

10 The macropore structure can also be controlled by adjusting the sintering pressure and temperature. The use of high pressures and hot pressing techniques will reduce macro pore volume. It is generally desirable to add a lubricant when using tabletting or extrusion equipment. The use of such lubricants is conventional in tabletting and extrusion technology. However, careful selection of lubricant is desirable to avoid adverse effects on the strength of the formed articles. It has been found that pellets made using 15 stearic acid as lubricant are substantially weakened, whereas the use of polyethylene glycol as lubricant has no effect on pellet strength.

When the amount of curing agent (eg hexamine) used in the initial partial cure step is insufficient for complete cure, further curing agent can be added prior to the forming stage. After forming the shaped article may be subjected to a post-curing step in which it is heated at temperatures of for example 120 to

20 170 °C, to complete the sintering.

The sintering step of the present invention may be carried out by applying heat to the phenolic resin particles, by applying pressure, or by a combination of both.

The addition of curing agent at the forming stage enables less curing agent to be added at the partial curing stage. This makes control of the initial partial curing easier. The sintering and forming steps may be

25 combined when the forming step is carried out at sufficiently high pressures. For forming steps carried out at pressures below 50 MPa at normal ambient temperatures (e.g. 10-30 °C) it will be necessary to carry out a subsequent heating (or post-cure) step to achieve the necessary sintering and it will be preferable to add additional curing agent at the forming step.

30 The carbonisation is carried out by heating the shaped articles at temperatures above 600 °C. The duration of the heating step may be for example 1 to 48 hours. The carbonisation step is carried out under an inert atmosphere or in a vacuum in order to avoid combustion of the carbon.

When making carbonised articles it is possible to carry out sintering and then carbonisation in a single heating step. However it is possible to use relatively simple equipment for the sintering step, while it may be desirable to use more complex apparatus e.g. rotary furnaces for carbonisation. The sintering step 35 enables a product to be obtained, using relatively simple apparatus, which is sufficiently strong to enable it to withstand the forces imposed on it by such rotary ovens.

30 The carbonisation step produces a reduction in the overall dimensions of the formed article being carbonised. This reduction is substantial at higher temperatures (i.e. greater than 700 °C) Nevertheless we have found it possible to produce carbonised articles which accurately reproduce the shape of a mould, even though the final dimensions of the article are considerably smaller than those of the mould.

An advantage of the present invention is that high heating rates can be used for carbonisation while maintaining a controlled open porosity.

The invention will now be described by reference to the following experiments, in which comparative tests, not according to the invention, are identified by letters, and Examples of the invention are identified 45 by numbers.

The phenolic resin used in Examples 1-12 was a phenol-formaldehyde novolak resin supplied by BP Chemicals under the designation J1011/H which contains 10% hexamine by weight and is in finely ground form 98% at less than 75 micrometres. Lower percentages of hexamine were obtained by adding a phenol-formaldehyde novolak resin supplied by BP Chemicals under the designation J1010 which consists of 50 ground resin alone.

Comparative Test A

This Comparative Test, not according to the invention, shows what happens when an attempt is made 55 to make a shaped article by directly casting the article from a phenolic resin and then attempting to carbonise the article directly without grinding and compacting. Direct casting of the article might seem the obvious method of producing an article with controlled shape.

Cylindrical dies 12 mm in diameter and 20 mm deep were filled with the curable powder composition of resin and 10% hexamine (J1011/H). The cylindrical blocks of resin were cured in the dies for 2.5 hours at 150 °C. After curing they were removed from the dies and carbonised by heating to 880 °C at a rate of 3.3 C/min and holding for 1.2 hours. The resulting objects were mishapen and contained large cavities.

5

Comparative Test B

10

This comparative test, not according to the invention, shows what happens when an attempt is made to make a shaped article from an uncured resin hexamine powder mixture. The curable composition was used as in Test A. 10% stearic acid was added and the powder was formed into 3/16" (4.8 mm) diameter pellets using a pressure of 550 MPa. These pellets were carbonised by heating to 800 °C at a rate of 5 °C/min. The pellets were found to have flowed together into a solid mass during carbonisation.

15

Comparative Test C

20

This comparative test, not according to the invention, shows what happens when an attempt is made to make a shaped article from a highly cured resin hexamine mixture. A 5% hexamine in resin mixture was prepared by mixing equal parts of J1011/H and J1010. This powder was placed in a tray and cured for 8 hours at 150 °C. The resulting solid was comminuted and the powder fraction less than 106 micrometres was taken. This was formed into pellets as in Test B. These pellets had a mean diametric crush strength of 2.2 N/mm (0.22 kg/mm). Posture of the green pellets gave a diametric crush strength of 0.3 N/mm (0.03 kg/mm). The pellets were carbonised as in Test B. After carbonisation the pellets had a mean diametric crush strength of 2.2 N/mm (0.22 kg/mm) showing that sintering in accordance with the invention had not taken place.

25

Example 1

30

Cylindrical blocks of resin were prepared of the same size and shape as in comparative test A but with the following differences. Resin J1011/H was poured into trays and cured for 2.5 hours at 150 °C. The resulting slabs of substantially but not completely cured resin were ground using a hammer mill to give particles with a size of 106-250 micrometres. The powdered resin was then mixed with 8% by weight of polyethylene glycol based on a total weight of composition to be pelleted and then formed into pellets in a hand press. The pressure applied was 260 MPa.

35

The resulting pellets were subjected to a postcuring step to sinter them by heating in an oven at 150 °C for 1 hour. The postcured pellets were then carbonised by heating to 900 °C at 5 °C/min. Although smaller in size the pellets were perfect cylinders and contained no large cavities when sectioned.

Examples 2, 3, 4

40

Experiments were carried out as in Comparative Test C but with the initial cure conditions being 120 °C for 2,4 and 8 hours respectively the results are given in Table 1. Crush strength of the green pellets decreases with increasing cure time.

45

Examples 5,6,7

Experiments were carried out as in Examples 2, 3 and 4 except that the resin was ground to a particle size of 106-250 micrometres. The results are given in Table 2. Crush strength of the green pellets decreases with increasing cure time.

50

Examples 8-12

55

These were carried out as in Examples 5-7 but with the initial cure, and post cure and carbonisation conditions as shown in Table 3. The results of crush strength measurements are shown in Table 3. In all cases sintering took place on pelleting and post curing sufficient to give strong porous carbon pellets after carbonisation. In the case of Examples 10 and 12 (in which stearic acid was used as lubricant) the strength of the resulting carbonised pellet was less than that obtained under the same conditions but using PEG as a pelleting lubricant.

Comparative Test D and E

This was carried out in the same way as Examples 9 and 10 except that a 10% hexamine was used at the partial cure stage. The conditions used are shown in Table 3. It was not possible to prepare pellets in 5 these experiments because of overcure of the phenolic resin in the initial cure stage.

Example 13

An experiment was carried out as in Tests D and E except that the phenolic resin used was a phenol-10 formaldehyde novolak resin not containing hexamine curing agent and sold by BP Chemicals Ltd under the identification J 1009/W. This was coarsely ground on the small scale (to less than 250 micrometres). Hexamine particles were mixed in with the resin before the initial curing stage. The conditions used and the results obtained are shown in Table 3. In this Example the extent of the initial cure has been controlled by the larger particle size and hence poorer dispersion of resin and hexamine. Regrinding of the partially cured 15 material has produced a powder capable of sintering under pressure to give strong pellets. These pellets have further sintered during the post cure step to give a very strong material.

Example 14

20 Finely ground phenolic resin containing 2.5-3.0% hexamine and sold by BP Chemicals under the identification J 11011/1 was cured for 2 hours at 150 °C. The resulting solid was ground to less than 106 micrometres. A mixture suitable for extrusion was prepared as follows:

2227 g - resin as prepared above
180 g - hexamine
25 240 g - poly ethylene glycol dissolved in 888g water
This mixture was blended in a Z-blade mixer for 10 minutes. The resulting material was extruded using a Russel Finex extruder, model EXDS-100. This material was dried in a fluid bed drier. The extrudate had a mean crush strength of 27 N/mm (2.7 kg/mm). The material was carbonised in nitrogen at 5 °C/min to 900 °C and held for 2 hours. The mean crush strength of the carbonised material was 19 N/mm (1.9 kg/mm).
30

Example 15

Phenolic resin containing 2.5-3.0% hexamine (J 11011/1) was cured for 2 hours at 150 °C. The resulting 35 solid was ground to 106-250 micrometres. To 200 g of this powder was added 18 g polyethylene glycol dissolved in 70 g water. This blend was pressed in a die of diameter 30 mm at a pressure of 14 MPa to produce a disc of thickness 2 mm. This was removed from the die. A number of discs could therefore be readily made. The discs were post-cured at 150 °C for 1 hour. Strong porous resin discs were thus manufactured. Some of the discs were carbonised by heating in nitrogen to 900 °C at 5 °C/min and holding 40 for 30 minutes. Strong porous carbon discs were produced of diameter 24 mm.

Example 16

Phenolic resin containing 2.5-3.0% hexamine (J 11011/1) was cured for 2 hours at 150 °C. The resulting 45 solid was ground to 106-250 micrometres. The resin powder was poured into a glass tube of internal diameter 25 mm and vibrated to ensure good packing. The tube and contents were postcured at 150 °C for 1 hour. The glass tube was then removed leaving a strong porous resin rod. This was carbonised as in Example 15. A strong porous carbon rod was produced of diameter 19 mm.

Table 1

5% hexamine cure temp. 120°C. Ground to less than
106 micrometres. Stearic acid lubricant.

Example	2	3	4
Cure time (hours)	2	4	8
Diametric crush strengths (kg/mm)			
"Green" Pellets	0.76	0.42	0.18
Postcured	*	0.55	0.36
Carbonised	*	1.86	1.92

15 + 0.1kg/mm = 1 N/mm

Table 2

20 As Examples 2-4 but with particle size 106-250 micrometre

Example	5	6	7
Cure time (hours)	2	4	8
Diametric crush strength (kg/mm)			
"Green" pellets	0.41	0.33	0.18
Postcured	-	0.48	-
Carbonised	-	-	-

25 30 In the above tables * indicates that the crush strength was
above 2 kg/mm.

35 + 0.1kg/mm = 1N/mm

40

45

50

55

Table 3

Experiment Resin	Initial Cure			Postcure Hours	Carbonisation	Crush Strength + Diameter kg/mm +	
	% Hexamine	Temperature °C	Time Hours			Raw	Postcured
8	2	150	4	8% Hexamine 10% PEG	170°C 2	800°C 10°C/min	1.21 12.90 8.25
9	4	150	4	6% HEX 10% PEG	150°C 1	900°C 10°C/min	0.77 8.24 7.23
10	4	150	4	6% HEX 10% Stearic Acid	150°C 1	900°C 10°C/min	0.23 2.51 2.38
D, E	10	150	4	(D) 10% PEG or (E) 10% Stearic Acid			
11	10	120	4	10% PEG	150°C 1	900°C 10°C/min	1.11 1.96 2.55
12	10	120	4	10% Stearic Acid	150°C 1	900°C 10°C/min	0.52 0.59 0.85
13	10	150	4	10% PEG	150°C 1	900°C 10°C/min	1.18 12.99 5.89

+ 0.1kg/mm = 1 N/mm

Claims

55

1. A process for the production of a shaped porous phenolic resin article with a continuous open pore structure which comprises:
 - (a) partially curing a phenolic resin to a solid,

- (b) grinding the solid to form particles,
- (c) forming the resulting ground product to a pre-determined shape at a pressure in the range 0 to 800 MPa,
- (d) sintering the shaped solid so as to produce a form-stable sintered product.

5 The temperature and duration of the partial curing step (a) being so selected as to give a degree of cure sufficient to give a sinterable product, and being such that a sample of the partially cured solid when ground to produce particles in the size range 106 - 250 micrometres and tabletted in a tabletting machine gives a pellet with a crush strength which is not less than 1N/mm.

- 10 2. A process for the production of a shaped porous carbon article with a continuous open pore structure which comprises forming a shaped porous phenolic resin article according to Claim 1, and carbonising the shaped porous phenolic resin article, the temperature and duration of the partial curing step (a) being such that the pellet after carbonisation has a crush strength of not less than 8N/mm.
- 15 3. A process according to either of Claims 1 or 2 wherein the degree of partial cure resulting from the partial curing step is sufficient to allow sintering of the comminuted phenolic resin particles without addition of cross-linking agent to the comminuted resin.
- 20 4. A process according to any one of the preceding claims wherein the phenolic resin is a phenol-formaldehyde resin.
- 5. A process according to Claim 4 wherein the resin is a novolak resin.
- 25 6. A process according to Claim 5 wherein the novolak resin is a hexamethylenetetramine-cured novolak resin.
- 7. A process according to Claim 6 wherein 5 to 10% of finely ground hexamethylenetetramine is mixed with finely ground novolak resin and the partial curing step on the resulting mixture is carried out at below 150 °C.
- 30 8. The process according to any one of the preceding claims wherein the partially cured resin is comminuted to a particle size less than 500 micrometres.
- 9. The process according to any one of the preceding claims wherein the shaped articles are formed by application of a pressure below 800MPa.
- 35 10. The process according to any one of claims 1 to 8 wherein the shaped articles are formed without the application of pressure.
- 40 11. The process according to any one of the preceding claims wherein polyethylene glycol is added to the phenolic resin before the forming step.
- 12. A process according to any one of the preceding claims wherein additional curing agent is mixed with the comminuted phenolic resin subjected to the forming step.
- 45 13. A process according to any one of the preceding claims wherein the shaped article resulting from the forming step is heated to 120 °C to 170 °C to complete the sintering.
- 14. A process according to claim 2 and any one of claims 3 to 13 as dependent on Claim 2 wherein the shaped articles are carbonised at temperatures above 600 °C.
- 50 15. A process according to claim 14 wherein the duration of the carbonisation step is 1 to 48 hours.

Patentansprüche

55

- 1. Verfahren zur Herstellung eines geformten, porösen Phenolharz-Artikels mit einer kontinuierlich-offenen Porenstruktur, welches umfaßt:
 - a) teilweises Härt(en) eines Phenolharzes zu einem Feststoff,

b) Mahlen des Feststoffs, um Teilchen zu bilden,

c) Formen des erhaltenen, gemahlenen Produkts zu einer vorbestimmten Form bei einem Druck von 0 bis 800 MPa,

d) Sintern des geformten Feststoffs, um so ein formstables, gesintertes Produkt zu bilden,

5 wobei die Temperatur und die Dauer der Stufe a) des teilweisen Härtens derartig ausgewählt sind, daß man einen Härtungsgrad erreicht, der zum Erhalten eines sinterfähigen Produkts ausreichend ist und sie sind derartig, daß eine Probe des teilweise gesinterten Feststoffs beim Mahlen, zur Bildung von Teilchen in einem Größenbereich von 106 -250 µm, und beim Tablettieren in einer Tablettierungsma-
schine ein Pellet mit einer Bruchfestigkeit von nicht weniger als 1 N/mm ergibt.

10 2. Verfahren zur Herstellung eines geformten, porösen Artikels aus Kohlenstoff mit einer kontinuierlich-
offenen Porenstruktur, welches das Formen eines geformten, porösen Artikels aus Phenolharz gemäß
Anspruch 1 umfaßt und das Carbonisieren des geformten, porösen Artikels aus Phenolharz, wobei die
Temperatur und die Dauer der Stufe a) des teilweisen Härtens derartig sind, daß das Pellet nach der
15 Carbonisierung eine Bruchfestigkeit von nicht weniger als 8 N/mm hat.

3. Verfahren nach Anspruch 1 oder 2, worin der Grad der teilweisen Härtung, der sich aus der Stufe der
teilweisen Härtung ergibt, ausreichend ist, um ein Sintern der zermahlenen Phenolharzteilchen ohne
Hinzugabe von Vernetzungsmittel zum zermahlenen Harz zu erlauben.

20 4. Verfahren nach einem der vorhergehenden Ansprüche, worin das Phenolharz ein Phenol-Formaldehyd-
harz ist.

5. Verfahren nach Anspruch 4, worin das Harz ein Novolak-Harz ist.

25 6. Verfahren nach Anspruch 5, worin das Novolak-Harz ein mit Hexamethylenetetramin gehärtetes Novolak-
Harz ist.

30 7. Verfahren nach Anspruch 6, worin 5% bis 10% fein gemahlenen Hexamethylenetetramins mit fein
gemahlenem Novolak-Harz vermischt wird und die Stufe der teilweisen Härtung der sich ergebenden
Mischung unterhalb 150 °C durchgeführt wird.

8. Verfahren nach einem der vorhergehenden Ansprüche, worin das teilweise gehärtete Harz zu einer
Teilchengröße von weniger als 500 µm zermahlen wird.

35 9. Verfahren nach einem der vorhergehenden Ansprüche, worin die geformten Artikel durch Anwendung
eines Druckes unterhalb von 800 MPa geformt werden.

40 10. Verfahren nach einem der Ansprüche 1-8, worin die geformten Artikel ohne Anwendung von Druck
geformt werden.

11. Verfahren nach einem der vorhergehenden Ansprüche, worin Polyethylenglycol zum Phenolharz vor der
Formbildungsstufe hinzugegeben wird.

45 12. Verfahren nach einem der vorhergehenden Ansprüche, worin ein zusätzliches Härtungsmittel mit dem
zerkleinerten Phenolharz, das der Formbildungstufe unterworfen wird, vermischt wird.

13. Verfahren nach einem der vorhergehenden Ansprüche, worin der geformte Artikel, der sich aus der
Formbildungsstufe ergibt, auf 120 °C bis 170 °C erhitzt wird, um das Sintern zu vervollständigen.

50 14. Verfahren nach Anspruch 2 und nach einem der Ansprüche 3 bis 13 - als Unteransprüche des
Anspruchs 2 -, worin die geformten Artikel bei Temperaturen von über 600 °C carbonisiert werden.

15. Verfahren nach Anspruch 14, worin die Dauer der Carbonisierungsstufe 1 bis 48 Stunden beträgt.

55

Revendications

1. Procédé pour la production d'un article mis en forme en résine phénolique poreuse, ayant une structure poreuse ouverte continue, qui comprend les étapes consistant:
 - 5 (a) à durcir partiellement une résine phénolique en un solide;
 - (b) à broyer le solide pour former des particules;
 - (c) à façonner le produit broyé résultant sous une forme pré-déterminée sous une pression comprise entre 0 et 800 MPa;
 - (d) à friter le solide mis en forme afin de produire un produit fritté de forme stable,

10 la température et la durée de l'étape de durcissement partiel (a) étant choisies de façon à donner un degré de durcissement suffisant pour obtenir un produit fritté, et étant telles qu'un échantillon du solide partiellement durci quand il est broyé pour produire des particules ayant une granulométrie comprise entre 106 et 250 micromètres et comprimé dans un appareil de moulage par compression, donne un granulé ayant une résistance à l'écrasement qui n'est pas inférieure à 1N/mm.
- 15 2. Procédé pour la production d'un article mis en forme en carbone poreux, ayant une structure poreuse ouverte continue, qui consiste à mettre en forme un article en résine phénolique poreuse selon la revendication 1, et à carboniser l'article mis en forme de résine phénolique poreuse, la température et la durée de l'étape de durcissement partiel (a) étant telles que le granulé après carbonisation, possède une résistance à l'écrasement qui n'est pas inférieure à 8 N/mm.
- 20 3. Procédé selon la revendication 1 ou 2, dans lequel le degré de durcissement partiel obtenu dans l'étape de durcissement partiel est suffisant pour permettre le frittage des particules de résine phénolique broyée sans ajouter d'agent de réticulation à la résine broyée.
- 25 4. Procédé selon l'une quelconque des revendications précédentes, dans lequel la résine phénolique est une résine phénol-formaldéhyde.
5. Procédé selon la revendication 4, dans lequel la résine est une résine novolak.
- 30 6. Procédé selon la revendication 5, dans lequel la résine novolak est une résine novolak durcie par l'hexaméthylènetétramine.
7. Procédé selon la revendication 6, dans lequel 5 à 10% d'hexaméthylènetétramine finement broyée sont mélangés avec la résine novolak et l'étape de durcissement partiel du mélange résultant est effectuée au-dessous de 150 °C.
- 35 8. Procédé selon l'une quelconque des revendications précédentes, dans lequel la résine partiellement durcie est broyée à une granulométrie inférieure à 500 micromètres.
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel les articles mis en forme sont préparés par application d'une pression inférieure à 800 MPa.
- 40 10. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel les articles mis en forme sont préparés sans l'application de pression.
11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polyéthylèneglycol est ajouté à la résine phénolique avant l'étape de mise en forme.
- 50 12. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'agent de réticulation supplémentaire est mélangé avec la résine phénolique broyée soumise à l'étape de mise en forme.
13. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'article mis en forme provenant de l'étape de mise en forme est chauffé à une température de 120 °C à 170 °C pour terminer le frittage.
- 55 14. Procédé selon la revendication 2 et l'une quelconque des revendications 3 à 13, dépendantes de la revendication 2, dans lequel les articles mis en forme sont carbonisés à des températures au-dessus

EP 0 254 551 B1

de 600 ° C.

15. Procédé selon la revendication 14, dans lequel la durée de l'étape de carbonisation est de 1 à 48 heures.

5

10

15

20

25

30

35

40

45

50

55